A HIGHLY ACCURATE *AB INITIO* DIPOLE MOMENT SURFACE FOR WATER: TRANSITIONS EXTENDING INTO THE ULTRAVIOLET

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We present a new *ab initio* dipole moment surface (DMS) for the water molecule valid for transitions which stretch into the near ultraviolet. Intensities computed using this surface agree very well with precise laboratory measurements designed to aid atmospheric observations. This work is based on a data set encompassing 17 628 multi-reference configuration interaction configurations that were calculated with the aug-cc-pCV6Z basis set with the Douglass-Kroll-Hess Hamiltonian to second order and required approximately 116 years of CPU running time to complete.

Compared to recent experimental measurements in the far infrared region[b], this new DMS significantly improves agreement with theory for transitions in the previously problematic bands (121), (300) and (102). For highly energetic overtones located in both the visible and ultraviolet regimes, we successfully predict the intensity of all measured bands to within 10% of the latest atmospheric observations[c]. These include bands at 487 nm (303), 471 nm (511), and 363 nm (900), for which previous models underestimated the intensity by up to 139%. Absorption features are also predicted in the 290 nm to 355 nm window and the theoretical shape demonstrates reasonably good behaviour with previously measured cross sections. The 10 ν_1 band is identified as the strongest absorber in this region and the maximum intensity is approximately 6.3×10^{-27} cm per molecule, which should be observable in atmospheric spectra.

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[b] M. Birk et al., J. Quant. Spectrosc. Rad. Transf, 203, 88-102 (2017)

[c] J. Lampel et al., Atmos. Chem. Phys, 17, 1271-1295, (2017)